

INDUSTRIAL APPLICATIONS OF GRAPHITE FLUORIDE FIBERS

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SUMMARY

Based on fluorination technology developed during 1934-1959, and the fiber technology developed during the 1970's, a new process was developed to produce graphite fluoride fibers. In the process, pitch based graphitized carbon fibers are at first intercalated and deintercalated several times by bromine and iodine, followed by several cycles of nitrogen heating and fluorination at 350-370°C. Electrical, mechanical, and thermal properties of this fiber depend on the fluorination process and the fluorine content of the graphite fluoride product. However, these properties are between those of graphite and those of PTFE (Teflon). Therefore, it is considered to be a semiplastic. The unique physical properties suggest that this new material may have many new and unexplored applications. For example, it can be a thermally conductive electrical insulator. Its coefficient of thermal expansion (CTE) can be adjusted to match that of silicon, and, therefore, it can be a heat sinking printed circuit board which is CTE compatible with silicon. Using these fibers in printed circuit boards may provide improved electrical performance and reliability of the electronics on the board over existing designs. Also, since it releases fluorine at 300°C or higher, it can be used as a material to store fluorine and to conduct fluorination. This application may simplify the fluorination process and reduce the risk of handling fluorine.

INTRODUCTION

Graphite fluoride is a product of elevated temperature fluorination of graphite. The graphite fluoride powder has been studied extensively for several decades since it was first reported in 1934 (Ref. 1, 2). The original objective of the present effort was to use this old knowledge of graphite fluorination, together with the new pitch-based graphitized carbon fibers (developed in the 1970's), to produce graphite fluoride fibers. These fibers could then be processed with the currently available fiber technology to make thermally conductive and electrically insulative products, which are useful in electrical or electronic industries for heat sinking purposes.

During the process of conducting this research, in order to reach the objective described above, the old knowledge of graphite fluorination needed to be augmented, and further development of the newly developed carbon fibers is needed. Also, based on the electrical, mechanical, and thermal properties of the graphite fluoride fibers thus obtained, many applications in addition to heat sinking are believe possible. In this report, the fluorination process and its effects on the physical properties of the graphite fluoride fiber products will be summarized, and the applications of the graphite fluoride fibers thus produced will be described.

GRAPHITE FLUORINATION PROCESS

Results of the study on graphite fluorination during 1934-1959 indicated that after contacting fluorine gas at 400-460°C temperature range, the planar molecular structure of graphite crystal (Figure 1a) became buckled, and carbon atoms were bonded to fluorine atoms covalently (Figure 1b) (Ref. 1, 2).

Figure 1b shows the molecular structure of a perfect graphite fluoride crystal whose fluorine to carbon ratio is 1.0. Such structure is seldom produced either in industry or in laboratory. This is because that, with direct contact of graphite crystals, the fluorine gas will either react only with the carbon atoms near the exterior region of the crystal at low temperature, or break the crystal structure in order to reach the interior carbon atoms at high temperature. Consequently, the graphite fluoride thus produced has less fluorine than carbon, and is structurally damaged.

In order to alleviate these problems, the graphite materials to be reacted with fluorine at high temperature were pre-tested with chemicals, called intercalants, which interleave between the carbon layers, to form an intercalated compound. The molecular structure of a typical intercalated compound is described in Figure 1c, in which bromine, the intercalant, is inserted into the space between the graphite planes. It is believed that the intercalants help to "open" the structure of the graphite material for fluorine to reach the carbon atoms near the center of the graphite crystal. This concept has been experimentally demonstrated (Ref. 3, 4).

The above concept suggests that the quality of the final graphite fluoride products depends not only on the graphite fluorination process, but also on the graphite pre-treatment process, or intercalation. The intercalation needs to be as complete as possible in order to eliminate pockets or pristine graphite, which would be the sources of structural damage, or defects, in the graphite fluoride fiber products. Also, the choice of intercalants needs to be such that it causes the least structural damage during intercalation. From the knowledge of graphite intercalation accumulated during the past 7 years of research at NASA Lewis Research Center, it was determined that bromine and iodine are the best intercalants for this purpose (Ref. 5, 6). Details on graphite intercalation with bromine and iodine are described in references 6 and 7.

The reaction of fluorine at 1 atm pressure and graphitized carbon fibers has been studied detail (Ref. 4, 9). The fluorine used in this work was pure commercially available fluorine containing 2-3% N_2 and HF. The effects of this impurity and the fluorine pressure on the fluorination process are not known. However, 1 atm HF was reported to react with graphite at 250° C (Ref. 2). It may act as a catalyst in the fluorination reaction. The fibers used in this work were mostly Amoco P-100 graphitized carbon fibers which contain 18% bromine by weight after bromine treatment. The P-100 fiber has interplanar spacing of 3.37 Å before bromine intercalation and 3.39 Å after bromine intercalation. Less graphitized carbon fibers were also used in a few experimental runs. This study concluded that the optimum reaction temperature is in the 350-370° C range for brominated P-100 fibers, and lower for less graphitized fibers. Also, the time needed for complete fluorination can be reduced if 2 or more cycles of nitrogen heating and fluorination at this temperature are conducted instead of a continuous fluorination process. It is believed that the nitrogen heating process helps to clear the pathway for fluorine to reach the carbon atoms near the center of the graphite crystals.

PROPERTIES OF GRAPHITE FLUORIDE FIBERS

The work done during 1934-1959 concluded that graphite fluoride was an electrical insulator having fluorine to carbon ratio of 1.0. However, the "complete fluorination" described in the last paragraph produced an electrically insulative fiber having fluorine to carbon atom ratio of 0.68 to 0.72. Further fluorination results in more structural defects but little increase in fluorine content in the products. The fact that the graphite fibers described here are electrical insulators but have much less fluorine than carbon suggests the formation of new carbon-carbon covalent bonds between the carbon atoms from the neighboring graphite layer (Ref. 8). However, it may also result from isolate double bond regions which could not be reached by fluorine during the fluorination reaction.

Some properties of the $CF_{0.68}$ graphite fluoride fibers were measured and are described in Table 1. It is noted that, with further optimization, the structural damage to the fibers during the fabrication process could be further reduced. Therefore, the thermal conductivity and the tensile strength of the fibers could increase.

The properties of pristine graphite fibers, graphite fluoride fibers, and fiber glass are compared in Table

1. It shows that the fiber properties change significantly as the fluoride content in the fibers changes from 0 to 0.68. Using the process described, partially fluorinated graphite fibers having fluorine content between 0 and 0.68 were also made. Further work concluded that partially fluorinated graphite fibers have physical properties between those of the pristine graphite fibers and those of the $CF_{0.68}$ fibers described in Table 1. The effect of the fluorine content on the fiber resistivity and the Young modulus are described in Reference 9. Quantitative study of the effect of fluorine content on the fiber CTE is time consuming and is not completed at this time. However, a clear trend of increasing CTE value with increasing fluorine content is observed. Also, after repeated experimental tests, the CTE value for the $CF_{0.68}$ graphite fluoride fibers is determined to be in the 2-7 ppm/ $^{\circ}$ C range. For comparison, the pristine graphitized carbon fiber has a CTE value of -1 ppm/ $^{\circ}$ C.

The physical properties of $CF_{1.0}$ described by previous scientists (Ref. 1, 2) were somewhat different from those of the $CF_{0.68}$ fibers described in Table 1. This again demonstrates that the physical properties of the graphite fluoride are strongly affected by the fluorine content in the graphite materials.

On the other hand, the physical properties of $CF_{1.0}$ are similar to those of PTFE (Teflon), whose chemical composition is approximately CF_2 .

Based on the experimental results described above, partially fluorinated graphite fluoride described in the report can be considered as a semiplastic.

Figure 2 shows the % weight loss after a $CF_{0.68}$ fiber sample was heated in air at different temperatures for 17, 24, and 192 hours. It shows that the weight of this graphite fluoride fiber sample changes very little under 200 $^{\circ}$ C air, but decreases slowly and continuously if the air temperature is 300 $^{\circ}$ C or higher. Data from ESCA and SEM's EDS suggest that the small amount of weight loss at 200 $^{\circ}$ C is not the result of loss of fluorine, but rather is due to the loss of a small amount of oxygen impurity in the fiber. On the other hand, the weight loss at 300 $^{\circ}$ C or higher is largely due to the loss of fluorine in the fibers (Ref. 10).

The electrical resistivity of graphite fluoride fibers, however, decreases from around 11 11 Ω -cm to around 10 6 Ω -cm. However, the graphite fluoride fibers do not react with anhydride-type epoxy hardener. The electrical resistivity of a composite made from such epoxy is found to be stable at room temperature and pressure, and is in the same range as that of the graphite fluoride fibers which made the composite.

APPLICATIONS OF GRAPHITE FLUORIDE FIBERS

The application of graphite fluoride fibers in space industry are summarized in Reference 11. Those applications are based on the unique properties of the graphite fluoride fibers described above. These properties, which can best be described as semiplastic, can certainly be used in other industries as well. As with any new fiber material, many new applications of the graphite fluoride fibers and its composites remain to be explored. However, some examples of the nonaerospace applications are described as follows.

Printed Circuit Board

Traditionally, the material used for printed circuit boards is fiberglass epoxy composites. Typically, it has CTE value of 7-13 ppm/ $^{\circ}$ C, and thermal conductivity of 0.3-0.4 W/M- $^{\circ}$ K.

The disadvantage of this CTE value is that it is somewhat different from the CTE value of silicon (3-7 ppm/ $^{\circ}$ C). The CTE mismatch generates stress on the pins of the silicon chip. As a result, if the device is operated over a wide temperature range, the joints between the pins and the board may crack, and the device becomes unreliable. This is especially true in the more advanced designs, where the silicon chips are large.

The disadvantage of the above described thermal conductivity value for fiberglass composites is that it is very low. Therefore, heat generated from conducting electricity through the electronics on the circuit boards

cause elevated device temperatures. Such high temperatures affects not only the electrical performance, but also the reliability because it enhances chemical corrosion, interfacial diffusion, and again, CTE mismatch (Ref. 12). This problem is especially true for the more advanced devices, where a large number of electronic components are packed in a small area.

The above disadvantages may be partially alleviated by using graphite fluoride fibers to replace fiberglass. For unidirectional graphite fluoride fiber-epoxy composites, the CTE and thermal conductivity values are estimated to be in the 3-6 ppm/ $^{\circ}$ C and 3-6 W/M- $^{\circ}$ C ranges, respectively, along the fiber directions. These values are better than those of fiberglass composites. In addition, further optimization of the fluorination process should result in even better CTE and thermal conductivity values.

Adhesion between metal and graphite fluoride is a concern for the use of graphite fluoride composites as a printed circuit board material. This property has not been studied in detail. However, letting a strand of graphite fluoride fibers, CF_{0.65}, be sandwiches between, and in direct contact with, two pieces of commercially available titanium foil at 200 $^{\circ}$ C for 2 hours, some fibers were found to adhere to the foils. This suggests that adhesion between graphite fluoride and titanium is possible. Using aluminum as the foil material and repeating the same experiment, the same phenomenon was observed, but to a lesser extent. The adhesion behavior observed here seems to be similar to that between metal and fluorocarbon as observed by Kid, et al (Ref. 13). However, more work is needed to understand and characterize this phenomenon.

Another factor important to the design of printed circuit boards made from graphite fluoride fibers is that the dielectric constant of the board needs to be low in order to allow signals to travel fast. The dielectric constant of graphite fluoride fibers, however, is not known at this time. However, it is believed that the impurities in the graphite fluoride fibers, i.e., oxygen, bromine, and iodine, need to be removed in order to have a product which contains no "conductive pockets" and, therefore, which has a minimum value of dielectric constant.

Fluorine Storage and Fluorination Agent

As described in Figure 2, partially fluorinated graphite fluoride losses fluorine if heated at 300 $^{\circ}$ C or higher. This prevents such graphite fluoride from being used at high temperatures. However, this also suggests that graphite can be used as a host material to store fluorine, and the partially fluorinated graphite fluoride can be used as a fluorination agent. Large amounts of highly reactive and toxic fluorine gas can be stored in the form of a solid, e.g., spools of graphite fluoride fibers which typically contain 50% fluorine by weight is easy to handle at room environment. Fluorine gas can then be released for use from this graphite fluoride by heating it at 300 $^{\circ}$ C or higher. The fluorine release rate can be controlled by adjusting the graphite fluoride heating temperature. An example of the possible use of this process in laboratory is to study the effects of fluorination on high temperature superconductors (Ref. 14). However, application of this process in industry, e.g., etching of amorphous silicon and silicon nitride thin films (Ref. 15), remains to be explored.

Other Applications

Some of the other applications of this new material that the authors believe possible are listed as follows:

- A lubricant (Ref. 16)
- The cathode material in lithium battery (Ref. 17)
- Insulators for windings of alternators
- Filler material which bonds to metal matrices to form a composite with strong traverse tensile strength

CONCLUSION

Graphite fluoride fibers with a fluorine to carbon atom ratio of 0.68 or lower were fabricated at NASA

Lewis Research Center. Physical properties of this material can be controlled to some extent by adjusting its fluorine content. For $CF_{0.88}$, the material behaves like a semiplastic. As with any new material, applications of the graphite fluoride fibers remain to be explored. However, it appears promising to use this material to fabricate heat sinking printed circuit boards which are CTE compatible with silicon. It also seems possible to use the graphite fiber as a host material to store fluorine gas, and to use the graphite fluoride fiber a safe fluorination agent.

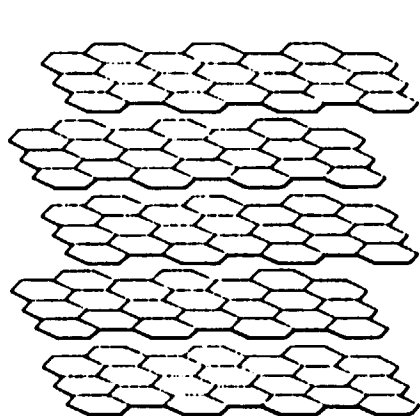
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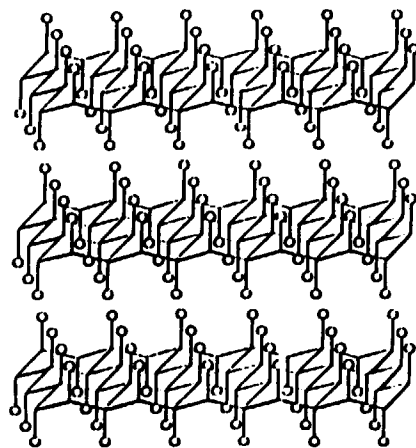
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Table 1 Physical properties of graphitized carbon fibers (P-100), graphite fluoride fibers ($\text{CF}_{0.68}$, made from P-100 fiber), and fiber glass (S type)

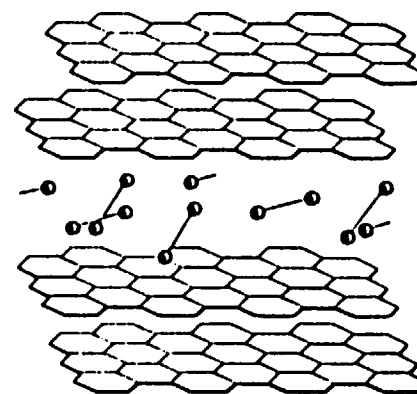
	Graphite fiber	Graphite fluoride	Fiber glass
Electrical resistivity ($\Omega\text{-cm}$)	2.5×10^{-4}	10^{11}	10^{14}
Thermal conductivity ($\text{W/M-}^\circ\text{K}$)	300	11	1.1
Young modulus (Msi)	105	25	12
Longitudinal tensile strength (Ksi)	300	40	500
Coefficient of thermal expansion ($\text{ppm/}^\circ\text{C}$)	-1	2-7	3
Density (g/cm^3)	2.18	2.5	2.5



A) GRAPHITE



B) GRAPHITE FLUORIDE



C) BROMINE INTERCALATED GRAPHITE

FIGURE 1 - MOLECULAR STRUCTURES

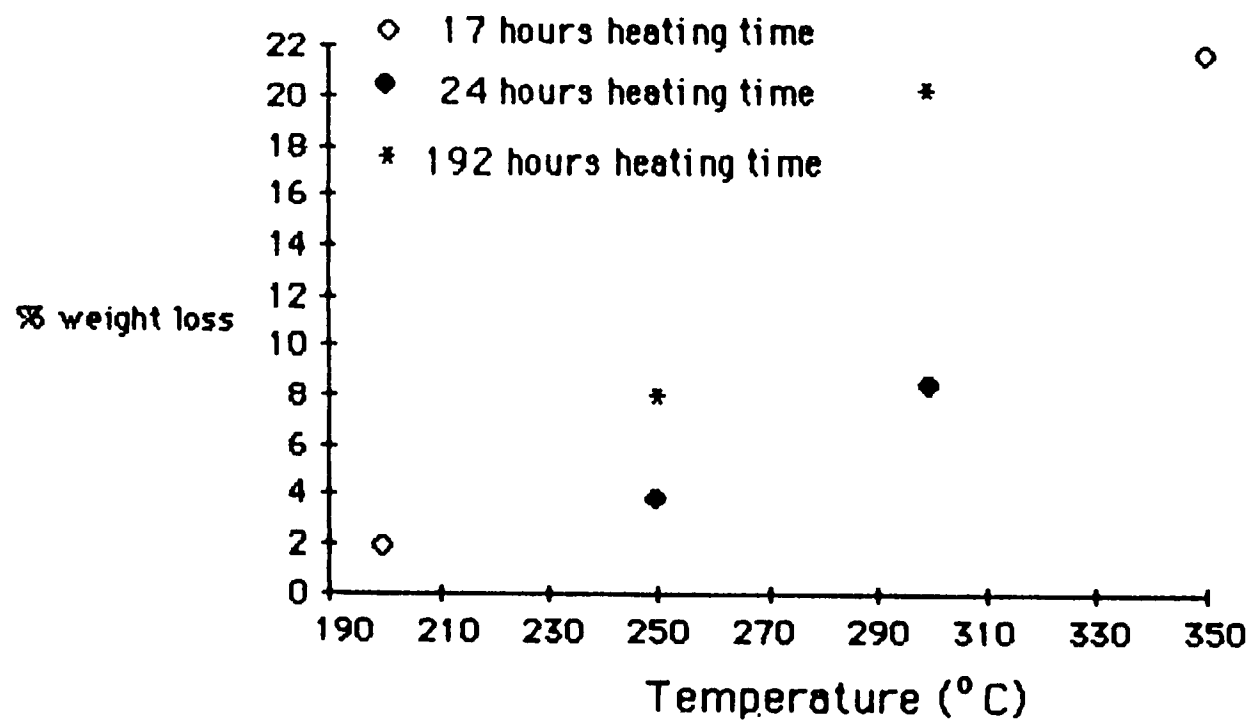


Figure 2 Weight loss after heating $CF_{0.65}$ in air